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High Performance of Chromium Recovery from Aqueous Waste Solution using Mixture of Palm-oil in Emulsion Liquid Membrane

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Abstract

Industrial effluent containing metal ions especially from semiconductor industry is considered as a serious environmental pollutant. A green emulsion liquid membrane (ELM) has been formulated in this research using an environmental-friendly refined palm oil as the main diluent of ELM to recover the chromium from wastewater. The feasibility of using palm oil–based ELM for chromium extraction and its stability were investigated. Several parameters, including carrier concentration, agitation speed, internal phase concentration, treat ratio, and agitation time, which could affect the extraction and recovery performance of chromium in ELM process, were attempted. The results showed that 0.2 M of TOMAC, 600 rpm for agitation speed and 1.0 M of NaOH, 2:1 for treat ratio provided enhancement of emulsion stability and almost 100% of chromium was extracted and recovered.

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Keywords: Emulsion liquid membrane; recovery; palm oil; chromium; semiconductor

1. INTRODUCTION

Semiconductor industry had a phenomenal growth in the past 25 years. Because of its tremendous growth, it is also facing several environmental issues [1]. According to Doble and Kumar [2], semiconductor manufacturing can be grouped broadly into three categories, which are silicon crystal wafer growth and preparation, semiconductor or

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wafer fabrication, and final assembly and packaging. The semiconductor fabrication processes are always performed in a clean room and include the following steps: oxidation, lithography, etching, doping (through processes such as vapour phase deposition and ion implantation), and layering (through processes such as metallization). There are some fabrication processes involving the removal and usage of chromium such as etching and electroplating (layering) steps. These steps will contribute to the presence of the chromium ions in semiconductor wastewater.In fact, there are two common stable forms of Cr present in environment, which are the trivalent Cr (III) and the hexavalent Cr (VI) species. Cr (III) and Cr (VI) have significant differences in terms of charge, physicochemical properties as well as chemical and biochemical reactivity [3]. Generally, Cr (VI) is found to be more toxic to plants and animals than Cr (III) [4, 5]. Through the intake of food and drink or even the air, Cr (VI), which acts as an oxidizing agent, can enter the human body and form free radicals during the reduction of Cr (VI) to Cr (III) occurring inside the cell. The high concentration of Cr (III) formed can inhibit some metallo-enzyme systems [3]. The cellular metabolism of Cr (VI) can also cause both oxidative and non-oxidative forms of DNA damage [6]. Chromium also exhibits its mutagenic and carcinogenic properties, which could bring about lung, skin and stomach cancer as well as other chronic diseases [5, 6, and 7].

In 1968, emulsion liquid membranes (ELMs) were first applied to the separation of hydrocarbons [8]. The emulsion liquid membrane (ELM) separation technique has been regarded as an emerging technology with considerable potential for a variety of applications [9]. Recently, ELM technology has become a promising method to recover precious metals, even in a very low concentration, from industrial wastes [10]. In this case, the receiving phase or stripping agent is emulsified in an immiscible liquid membrane before dispersing in the feed solution. After that, mass transfer of solute from the feed to the internal stripping phase takes place [11]. Since the emulsion liquid membrane (ELM) process combines the extraction and recovery (or concentration) process, this method does not need a second treatment like electrowinning, which needs another treatment, which is cementation or chemical precipitation process [12, 13]. Due to its high surface area to volume ratio compared to solid membranes, high solute transfer flux and selectivity as well as low contacting equipment volume and cost [12, 14] was chosen as the suitable method to extract and recover chromium from semiconductor wastewater.

Nowadays, there are very few studies that use palm oil as a diluent in the ELM process. Yet, among nine types of commercially available vegetable oils in India, Venkateswaran and Palanivelu [15], found that palm oil is the best LM with permeability of 8.5×10−6 m/s in acidic feed of pH 2.0 with 0.2 M sodium hydroxide as an effective stripping agent. Since palm oil is easily available in Malaysia at a low cost, it is a suitable substitute for the common petroleum-based diluents such as kerosene, toluene, heptane and n-dodecane.

Hence, in this research, palm oil will be utilized as a naturally occurring and green liquid membrane for the recovery of chromium from the semiconductor wastewater. The feasibility of using palm oil based emulsion liquid membrane for chromium extraction and its stability were investigated. Furthermore, the effects of parameters which affect the extraction and recovery performance of chromium in ELM process are also presented in this paper.

2. EXPERIMENT

2.1 Materials

All the chemicals described here are used without any further purification. Span 80 (Sorbitan oleate or Sorbitan (Z)-mono-9-octadecenoate), as a non-ionic surfactant, and the mobile carrier or extractant, which is TOMAC, were received from Sigma-Aldrich Co., USA. The co-surfactant, 1-octanol was purchased from R&M Marketing, Essex, United Kingdom. Sigma-Aldrich Co., USA also kindly supplied kerosene of boiling point ranging from 175°C to 325 °C while the refined palm oil used, branded Buruh, was manufactured by Lam Soon Group. Sodium hydroxide pellets branded J.T.Baker® (assay: 98 %) was purchased from Avantor Performance Materials Sdn Bhd and potassium dichromate graded AR (assay: minimum 99.9 %) was procured from QReC (Asia) Sdn Bhd. The solution of sodium hydroxide and chromium of desired molarity were prepared by dissolving and mixing appropriate weight of pellets of sodium hydroxide and potassium dichromate respectively in specific amounts of de-ionized water.

2.2 Experimental Procedures

2.2.1 Preparation of primary emulsion (w/o)

Liquid membrane was prepared by mixing an appropriate amount of TOMAC, Span 80 and 1-octanol in a 30 mL beaker with 7.5 mL of organic phase (mixture of 30% kerosene and 70% palm oil). The mixture was stirred using

magnetic stirrer (Cole-Parmer, model: StableTemp Ceramic Stirring Hot Plate, 7" x 7", 120 VAC) to achieve a homogenous mixture. 2.5 mL of the internal phase, sodium hydroxide (NaOH) solution was added slowly into the membrane phase to produce primary emulsion. Before the addition of the internal phase, the high speed homogenizer (Heidolph, model: SilentCrusher M) was switched on at the speed of 5000 rpm and the mixture was homogenized for another 0.5 min after adding all the internal phase. Besides, in this experiment, 1-octanol was used as the fixed co-surfactant or modifier to achieve a more stable ELM. The presence of 1-octanol can provide more efficient packing of the surfactants in the water in oil (W/O) interfaces as the repulsion of the hydrophilic head-groups of the surfactants can be minimized [16].

2.2.2 Chromium Extraction Experiment

ELM extraction of chromium was carried out by dispersing the W/O emulsion into the external phase containing Cr ions. The water in oil in water (W/O/W) emulsion was agitated using a four-blade stirrer (Cole-Parmer, model: 50006-00). Several parameters such as carrier concentration, agitation speed, internal phase concentration, treat ratio, and agitation time were varied during the chromium extraction experiments. After the extraction process, the sample mixture of W/O emulsion and external phase was separated using separating funnel. The aqueous external samples was analysed using Atomic Absorption Spectroscopy (PerkinElmer, model: Analyst 400) for chromium removal extraction performance.

The percentage of Chromium extraction, recovery and swelling or breakage was determined by using Eq. 1, 2 and 3, respectively:

$$\text{Extraction (\%)} = [([Cr]_i - [Cr]_f) / [Cr]_i] \times 100\% \quad (1)$$

$$\text{Recovery (\%)} = [Cr]_{int}/(2TR[Cr]_i) \times 100\% \quad (2)$$

$$\text{Swelling/Breakage (\%)} = (V_f - V_i)/V_i \times 100\% \quad (3)$$

where, $[Cr]_i$ is the initial concentration of Cr ion in aqueous before extraction, $[Cr]_f$ represents the final concentration of Cr ion in aqueous after extraction, $[Cr]_{int}$ is the concentration of Cr in internal phase after extraction, V_i is the initial volume of emulsion before extraction, V_f is the final volume of emulsion after extraction, and TR is the treat ratio.

3. RESULTS AND DISCUSSION

3.1 Mechanism of Chromium Extraction Process

In this work, Tri-n-octylmethylammonium chloride (TOMAC) (NR4+Cl−, where R = (CH2)6CH3) was used as the extractant or carrier in the membrane phase. Prior to the extraction reaction, TOMAC diffused through the membrane to the membrane-internal interface where it reacted with the stripping agent, NaOH as shown in Reaction 4. Thus, there were actually two types of extractants presented in the membrane phase to react with the chromium anionic complex, the TOMAC (NR_4+Cl−) and TOMAOH (NR_4+OH−) [16, 17, 18, 19, and 20).

$$NR_4^+Cl^- + NaOH \rightleftharpoons NR_4^+OH^- + Cl^- + Na^+ \quad (4)$$

Besides, chromium (VI) stock solution used in the experiment was prepared by dissolving potassium dichromate salt in de-ionized water. Generally, hexavalent chromium ions exist in aqueous solution as various forms of chromate such as hydrochromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ionic species. According to Grevatt, (1998) the proportion of each ion in solution is pH dependent. At basic and neutral pH, the chromate (CrO_4^{2-}) ions predominate. When the pH of the chromium solution is lowered (6.0 to 6.2), the concentration of hydrochromate ($HCrO_4^-$) ions increases. In very acidic condition, the dichromate ($Cr_2O_7^{2-}$) species predominate. In this experiment, pH of the chromium (VI) stock solution prepared was around 6.0 and, thus, hydrochromate ($HCrO_4^-$) ions predominated and involved in most of the reactions.

Therefore, both the extractants ($NR_4^+Cl^-$ and $NR_4^+OH^-$) reacted with $HCrO_4^-$ to form a Cr-carrier complex (NR_4HCrO_4) at the external interface through reversible ion-exchange reaction as shown in Reactions 5 and 6 [20].

$$NR_4^+Cl^- + HCrO_4^- \rightleftharpoons NR_4HCrO_4 + Cl^- \quad (5)$$

$$NR_4^+OH^- + HCrO_4^- \rightleftharpoons NR_4HCrO_4 + OH^- \quad (6)$$

The complex NR_4HCrO_4 diffused through the membrane phase and reached the internal (water-in-oil) interface where it reacted with the stripping agent (NaOH) to release the hydrochromate ($HCrO_4^-$) anion and carrier. Besides, chloride anions which were present in the internal phase due to the Reaction 1 could also contribute towards the stripping of hydrochromate anions. Consequently, the stripping reaction yielded the $Na^+HCrO_4^-$ salt and carrier as shown in Reactions 7 and 8. $Na^+HCrO_4^-$ is insoluble in the membrane phase and, thus, it would remain trapped in the internal droplets. The carrier recovered in the reactions travelled back to the external interface and continued to extract the $HCrO_4^-$ ion in external phase. Due to the high pH (basic) condition in internal phase, the $HCrO_4^-$ ion would dissociate and remain in equilibrium with the CrO_4^{2-} ion as shown in Reaction 9 [20].

$$NR_4HCrO_4 + NaOH \rightleftharpoons Na^+HCrO_4^- + NR_4^+OH^- \quad (7)$$
$$NR_4HCrO_4 + Na^+Cl^- \rightleftharpoons Na^+HCrO_4^- + NR_4^+Cl^- \quad (8)$$
$$HCrO_4^- + OH^- \rightleftharpoons CrO_4^{2-} + H_2O \quad (9)$$

In addition, as the extraction and stripping process proceeded, the hydroxide ions were released into the external phase through Reaction 6 and pH of external phase increased [16]. As the pH changed, amount of CrO_4^{2-} ions increased and consequently reacted slowly with $NR_4^+Cl^-$ and $NR_4^+OH^-$ as shown in Reactions 10 and 11. The stripping reactions of CrO_4^{2-} ions are depicted in Reactions 12 and 13.

$$2\,NR_4^+Cl^- + CrO_4^{2-} \rightleftharpoons (NR_4)_2CrO_4 + 2\,Cl^- \quad (10)$$
$$2\,NR_4^+OH^- + CrO_4^{2-} \rightleftharpoons (NR_4)_2CrO_4 + 2\,OH^- \quad (11)$$
$$(NR_4)_2CrO_4 + 2\,NaOH \rightleftharpoons Na_2CrO_4 + 2\,NR_4^+OH^- \quad (12)$$
$$(NR_4)_2CrO_4 + 2\,Na^+Cl^- \rightleftharpoons Na_2CrO_4 + 2\,NR_4^+Cl^- \quad (13)$$

Overall, the mechanisms of chromium extraction and stripping process involving the $HCrO_4^-$ ion TOMAC and NaOH are illustrated in Figure 1.

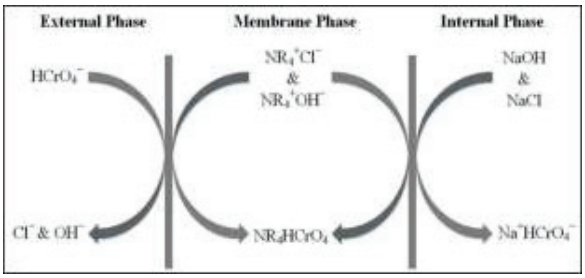

Fig 1 Extraction and stripping mechanism of Cr by TOMAC

3.2 Emulsion Stability and Chromium Extraction Performance

3.2.1 Effect of Carrier (TOMAC) Concentration

In this present work, TOMAC has been selected as the carrier in an organic phase that consisted of 30 % by volume from kerosene and 70 % from palm oil. Figure 2 depicts the experimental results of chromium extraction. Apparently, with an increasing carrier concentration from 0.01 M to 0.1M, there is more Cr-carrier complex that can be formed and, hence, the percentage of chromium extracted from feed phase increases gradually. As shown in Figure 2, 0.1 M TOMAC and above provide better extraction performance because they are able to extract almost 100% of chromium. This result is in line with Chakraborty *et al.*, [19] who also used high concentration of TOMAC of around 0.18 M.

However, instead of 0.1 M TOMAC, 0.2 M TOMAC had been chosen as the optimum concentration of carrier in this case because it could increase the viscosity of the ELM as shown in Figure 3. According to Karimi and Björkegren (2012), high viscosity of ELM can help to enhance the stability of the ELM so that it would not

swell or break easily during the extraction stage. Low TOMAC concentration such as 0.01 M and 0.05 M did not increase much of the ELM viscosity. Hence, the ELM is quite unstable and breakage of ELM occurred as shown in Figure 2. In addition to that, at the end of extraction, ELM with the presence of 0.2 M TOMAC did undergo swelling but the extent of ELM swelling in the presence of 0.1 M TOMAC was more obvious.

Besides that, increasing the concentration of TOMAC over a certain limit can cause the osmotic pressure to become higher in ELM than in the external phase [18, 21] and, thus, a very obvious swelling phenomena occurred as water entered the ELM for the case of 0.4 M and 0.6 M of TOMAC. Too high amount of carrier present in the ELM could also bring about the increment in mass transport resistance [17] and the Cr (VI) extraction percentage decreased consequently for 0.4 M and 0.6 M TOMAC. Therefore, 0.2 M TOMAC was chosen as a better carrier concentration to proceed to the extraction study.

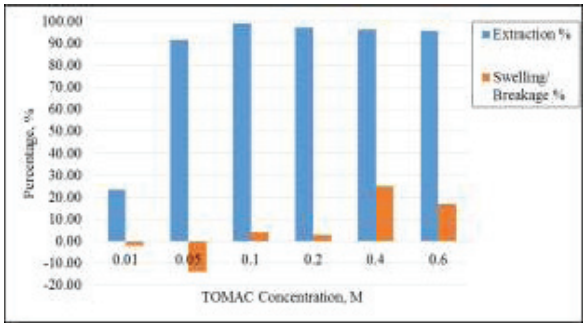

Fig 2 Chromium extraction percentage and ELM swelling percentage (TOMAC concentration) [Experiment conditions: agitation time = 2 min, agitation speed = 600 rpm, ratio of kerosene: palm oil = 3:7, [NaOH] = 0.1 M, [Span 80] = 3 % w/v, ratio of organic: NaOH = 3:1 and treat ratio = 2:1]

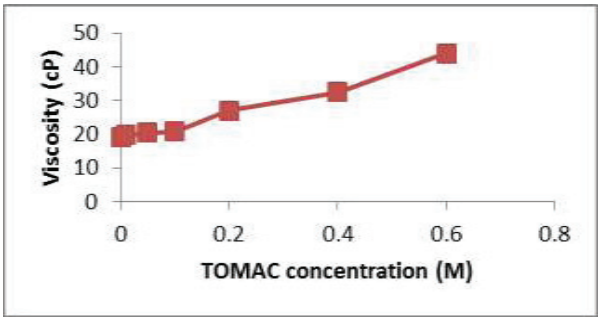

Fig 3 Effect of carrier concentration on viscosity of liquid membrane (Experimental conditions: ratio of kerosene: palm oil = 3:7)

3.2.2 Effect of Agitation Speed

In order to find out the optimal agitation speed that allows emulsion stability and effectiveness chromium (VI) extraction, the effect of agitation speed was investigated in the range of 200 till 800 rpm and the results obtained are analyzed as shown in Figure 4. The results show that agitation speed of 200 rpm provided a higher extraction percentage with less swelling (3 %) than 400 rpm. However, due to the low agitation speed of 200 rpm, the ELM globules cannot be well-dispersed in the external solution and formations of large globules were observed during the experiment. This result is in agreement with Kumbasar [21], who attempted the extraction of chromium (VI) using kerosene-based ELM at agitation speed of 350 rpm instead of 275 rpm. Hence, 200 rpm should not be chosen as the suitable agitation speed.

Next, when the agitation speed was increased from 400 rpm to 800 rpm, there was a gradual increment in the chromium extraction percentage from 92 % to 97 % as shown in Figure 4. Higher stirring rate can facilitate the formation of smaller sized ELM globules, thereby increasing the interfacial area between the feed solution and the

emulsion liquid membrane solution, which leads to an increase in the mass transfer rates as well as the chromium (VI) extraction efficiency [17, 22, 23].

Comparing between two high agitation speeds of 600 rpm and 800 rpm, both sets of the experiment achieved considerably high chromium extraction percentage of about 97 %. However, in this case, 600 rpm is more preferable than 800 rpm as the agitation speed. This result is in line with Karimi and Björkegren [16], who claimed that 600 rpm is the minimum agitation speed for a pure palm oil–based ELM to be dispersed in small sizes when contacting the external phase with ELM due to the high viscosity of ELM. As shown in Figure 4, when agitation speed of 800 rpm was applied in the experiment, swelling percentage also became larger than that of 600 rpm. This indicates that agitation speeds that exceed a certain limit could also bring about the swelling of ELM due to the increasing rate of co-transport of water and this might cause the ELM to become highly unstable [21, 24]. Hence, 600 rpm was considered to be the optimal agitation speed to provide a good dispersion of ELM globules along with the least possibility of breakage. To further the study of ELM extraction and Chromium recovery, selected conditions of stable emulsions of 0.2 M TOMAC and 600rpm agitation speeds were used.

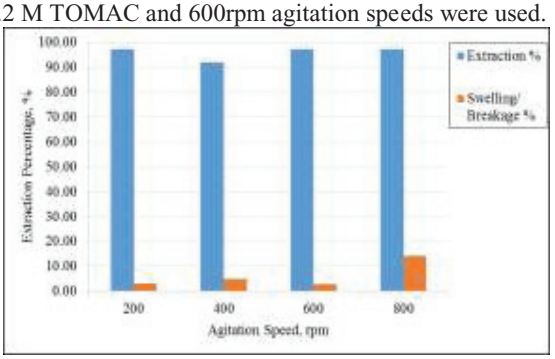

Fig 4 Chromium extraction percentage and ELM swelling percentage (Agitation speed) [Experiment conditions: agitation time = 2 min, ratio of kerosene: palm oil = 3:7, [NaOH] = 0.1 M, [TOMAC] = 0.2 M, [Span 80] = 3 % w/v, ratio of organic: NaOH = 3:1 and treat ratio = 2:1]

3.2.3 Effect of NaOH Concentration on Chromium Recovery

In this experiment, the sodium hydroxide solution acted as the stripping phase and its concentration was considered as one of the parameters that could affect the recovery efficiency of ELM. Figure 5 shows the effect of NaOH concentration on the chromium extraction performance. The highest chromium extraction percentage can be achieved using 0.1 M NaOH but it provides the lowest chromium recovery percentage. It is due to the insufficiency of stripping agent to strip out the chromium into the internal phase. Further increment of NaOH concentration to 0.5 M enhances the recovery of chromium but the extraction percentage decreases. With an increase of NaOH concentration from 0.5 M to 1.0 M, there is a great improvement in the chromium (VI) removal efficiency from 75 % to 93 %. This is due to the fact that higher concentration of NaOH can provide more OH^- and, hence, more Cr ions in the form of Cr-carrier complex are able to be stripped on the inner (W/O) interface of ELM. The more the chromium being stripped, the more carrier molecules can be free from the Cr-carrier complexes and continue to facilitate the removal of chromium from external solution.

From the aspect of recovery percentage, the stripping effect of NaOH increased gradually as shown in Figure 5, 1 M of NaOH acted as the most effective stripping agent in extracting as well as concentrating the chromium (VI) transported through the organic phase. When the Cr-carrier formation rate is constant for each set of experiment due to the usage of the same amount of surfactant and carrier, the enhanced stripping rate at higher concentration of NaOH can be achieved by providing sufficient OH^- in the stripping phase to extract the Cr (VI) from the Cr-carrier complexes. Hence, at low concentration of NaOH, many Cr-carrier complexes still remain unstripped in the membrane phase. This will cause low recovery percentage of chromium.

Nevertheless, with the increase of NaOH concentration up to 2.0 M, the chromium removal efficiency and recovery rate dropped significantly. According to Goyal *et al.*,[17] the surfactant, Span 80 reacts with high concentration NaOH and thus, the effective number of surfactant molecules reduces and then the emulsion liquid membrane destabilizes. Breakage of ELM due to the ELM instability releases the stripped chromium back into the stripping phase. At the same time, high concentration of NaOH induces large difference in osmotic and pH pressure

as compared to the external phase [16, 18, and 24]. This consequently results in the swelling of the ELM, which also reduces the recovery efficiency. Hence, when the rate of swelling is equal to the rate of breakage, there will be no observable increase or decrease in the volume of external solution as in the case of 2 M of NaOH. Therefore, 1 M is the suitable concentration of NaOH as it possesses the greatest ability to strip and concentrate the chromium from the feed solution.

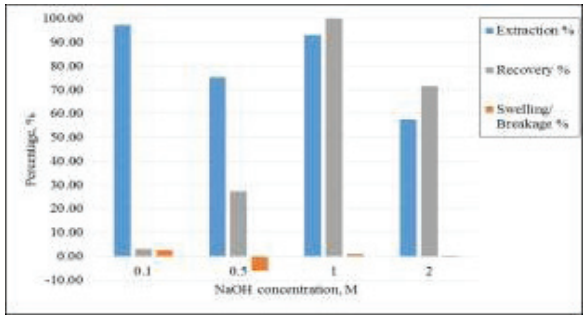

Fig 5 Chromium extraction percentage, chromium recovery percentage and ELM swelling percentage (NaOH concentration) [Experiment conditions: agitation time = 2 min, agitation speed = 600 rpm, ratio of kerosene: palm oil = 3:7, [TOMAC] = 0.2 M, [Span 80] = 3 % w/v, [1-octanol] = 2 % w/v, ratio of organic: NaOH = 3:1 and treat ratio = 2:1]

3.2.4 Effect of Treat Ratio on Chromium Recovery

Figure 6 shows the effect of treat ratio on chromium removal and recovery. The results present that emulsion liquid membrane (ELM) possesses greater ability to remove chromium (VI) ion from the feed phase when the lower treat ratios was applied (2:1). This is due to the fact that when the treat ratio is decreasing, the volume of ELM is comparatively increasing in the system and there will be more possible active sites on the membrane phase available for the chromium permeation process [23].

Furthermore, the ELM globules underwent swelling when treat ratio of 3:1 was applied and it might due to the osmotic pressure difference between the ELM and external phase. The increasing osmotic pressure difference could also bring about the rupture of ELM globule since breakage had occurred for the treat ratio of 5:1 and 10:1. The larger osmotic pressure difference between external and ELM phase when treat ratio increased was incurred by the presence of larger amount of water molecules in the external phase [17]. Hence, the percentage of chromium removal from the external phase and the percentage of chromium recovery decrease as compared to treat ratio of 2:1. Besides, Goyal *et al.* [17] also claimed that it is plausible that there is no sufficient free internal reagent, NaOH, to strip the chromium (VI) ion from the Cr-carrier complex in membrane phase. Meanwhile, the available carrier molecules at the O/W interface decreases and, thus, the percentage of chromium extracted also decreases.

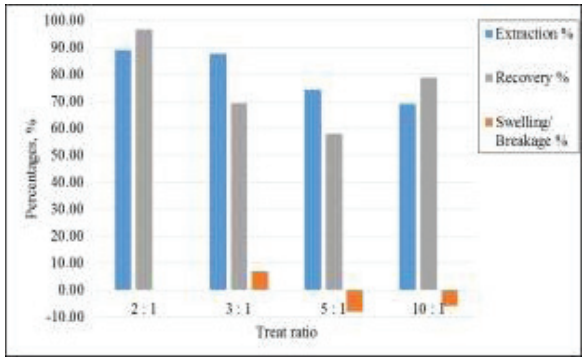

Fig 6 Chromium extraction percentage, chromium recovery percentage and ELM swelling percentage (Treat ratio) [Experiment conditions: agitation time = 2 min, agitation speed = 600 rpm, ratio of kerosene: palm oil = 3:7, [TOMAC] = 0.2 M, [NaOH] = 1 M, [Span 80] = 3 % w/v, [1-octanol] = 2 % w/v and ratio of organic: NaOH = 3:1]

In this study, the similar chromium removal percentages achieved using treat ratios of 2:1 and 3:1 implied that treat ratio of 3:1 would be the more economically effective choice in chromium extraction as less ELM is needed to treat the same amount of external phase. However, when the chromium recovery efficiency is considered, the higher chromium recovery percentage of 97 % can be achieved using treat ratio of 2:1 as compared to that of treat ratio of 3:1, which is only 69 %. Besides, when treat ratio of 2:1 was applied in the experiment, the ELM phase did not undergo such swelling or breakage problem as other treat ratios used in the extraction. Hence, it can be concluded that treat ratio of 2:1 is the best to be applied in the chromium extraction and recovery process.

4.0 CONCLUSION

In this work, the extraction and recovery of Cr by ELM using palm oil–based liquid membrane were investigated. Diluent containing kerosene-palm oil mixture with the ratio of 3:7 was selected and used. The influence of various parameters on the Cr extraction and recovery has been accepted and the results show that the optimum conditions were identified, such as 0.2 M for carrier (TOMAC) concentration, 600 rpm for agitation speed, 1.0 M for internal phase (NaOH) concentration, 2:1 for treat ratio and 3 minutes for agitation time in order to enhance the recovery of chromium in ELM process.

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